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**TITLE:** QUALITY ASSURANCE PROGRAM FOR SURVEILLANCE OF FAST REACTOR  
MIXED OXIDE FUEL ANALYTICAL CHEMISTRY

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SEMINAR ON NUCLEAR FUEL QUALITY ASSURANCE

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FAST REACTOR MIXED OXIDE FUEL ANALYTICAL CHEMISTRY

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ABSTRACT

An effective quality assurance program for the chemical analysis of nuclear fuel is essential to assure that the fuel will meet the strict chemical specifications required for optimum reactor performance. Such a program has been in operation since 1972 for the fuels manufactured for the Fast Flux Test Facility. This program, through the use of common quality control and calibration standards, has consistently provided high levels of agreement among laboratories in all areas of analysis. This paper gives a summary of the chemical specifications for the fuel and source material, an outline of the requirements for laboratory qualifications, the preparation of calibration and quality control materials, the general administration of the plan, and examples where the program has been useful in solving laboratory problems.

## INTRODUCTION

A comprehensive quality assurance program has been in operation since 1972 to assure that the chemical methods used for the analysis of fuel materials for the Fast Flux Test Facility (FFTF) reactor were in control. The FFTF is being constructed for the U. S. Energy Research and Development Administration (ERDA) as the major test reactor for the evaluation of components for the Liquid Metal Fast Breeder Reactor (LMFBR) program. The prime contractor for this facility is the Westinghouse Hanford Company operating the Hanford Engineering Development Laboratory (HEDL). As prime contractor, HEDL has the responsibility for the implementation of the quality assurance program. As an independent laboratory, the Los Alamos Scientific Laboratory (LASL) provides the calibration and quality control materials to all participating laboratories. These include the supplier of the source plutonium material, the fuel manufacturers, and HEDL the reactor operator.

This paper presents all aspects of the quality assurance program and gives examples of its successes and shortcomings during its three years of operating history. The topics covered are: (1) a summary of the chemical specifications for the fuel and source materials, (2) an outline of the requirements and tests for laboratory qualifications, (3) a discussion of the preparation, characterization, packaging, and record-keeping of the calibration and quality control materials. (4) administration of the program including the tabulating and charting of quality control sample analysis data to disclose problems unique to one laboratory or common to all laboratories, and (5) operational experiences.

## FUEL AND SOURCE MATERIAL SPECIFICATIONS

A FFTF fuel pin contains approximately 144 mixed uranium-plutonium oxide pellets, each about 1.2 g. The uranium to plutonium ratio is 3, the Pu-239 + Pu-241 isotopic abundance is 88%, and the uranium is natural or depleted. The fuel is highly refractory, being prepared at 1600°C in a hydrogen atmosphere to give a hypostoichiometric oxygen content. Each fuel pin also contains four uranium dioxide insulator pellets, two at each end. The source materials are ceramic grade uranium dioxide and plutonium dioxide. To increase the probability that the manufactured fuel meets specifications, the chemical specifications for the source materials are essentially the same as the chemical specifications for the finished fuel pellets. The chemical specifications for the source materials, the fuel, and the insulator pellets are given in Table I.

TABLE I. CHEMICAL SPECIFICATIONS FOR FFTF FUEL MATERIALS

Specification	Maximum Values (Unless Otherwise Stated)			
	Ceramic Grade UO <sub>2</sub>	Ceramic Grade PuO <sub>2</sub>	Mixed Oxide Fuel Pellets	Insulator Pellets
1. Pu Isotopic, wt %				
239 + 241		88.0±0.5	88.0±0.5	
241	Not applicable	2.5	2.5	Not applicable
238		0.15	0.15	
Sum others except 240		0.35	0.35	
240		balance	balance	
2. U Isotopic, wt % 235U	Natural or depleted		Natural or depleted	Natural
	0.71±0.05		0.71±0.05	0.71±0.05
3. Pu, wt %	Not applicable	Min. 85.0 at time of packaging Min. 87.5 after heat- ing to 920°C	+3.5 rel% of nominal value for indiv pellets; +1.0 rel% nominal value for lot average	Not applicable
4. U, wt %	Min. 86.6 dry basis	0.2	+1 rel % of actual content	None given
5. Americium, wt % of Pu	Not applicable	0.25	0.25	Not applicable
6. Carbon, µg/g	150	200	150	200
7. Chlorine µg/g	25	50	30	30
8. Fluorine, µg/g	25	25	10	10
9. Nitride Nitrogen, µg/g	200	200	200	200
10. Phosphorus, µg/g	50	200	100	100
11. Sulfur, µg/g	300	300	300	300
12. Gas, STP cc/g	None given	None given	0.09	0.09
13. Water, µg/g	5000	None given	20 for indiv pellets; 10 for lot average	20 for indiv pellets; 10 for lot average
14. Total Volatiles, wt %	None given	2.5	None given	None given
15. O/M Ratio	2.03 to 2.25	1.95 to 2.00	1.93 to 1.98 for individual 1.94 to 1.97 for average	1.995 to 2.010
16. Metal Impurities, µg/g				
Al	500	250	500	500
B	10	10	20	20
Be	20	20	20	20
Ca	100	500	250	150
Cd	20	20	20	20
Co	10	20	20	10
Cr	200	200	250	250
Fe	400	350	500	500
K	200	200	200	200
Li	10	10	10	10
Mg	25	100	25	25
Na	500	300	500	500
Ni	400	300	500	500
Ta	400	400	400	400
W	100	100	100	100
V	400	200	500	500
Cu, Si, Ti, Zn	500	500	500	500
Ag, Mn, Mo, Pb, Sn,	200	200	200	200
Dy, Eu, Gd, Sm	100	100	100	100

## REQUIREMENTS AND TESTS FOR LABORATORY QUALIFICATIONS

As previously stated, the analytical laboratories of the supplier of the plutonium source material, the fuel manufacturers, and HEDL, as the reactor operator, must qualify for all chemical analyses used to characterize these materials. Major qualification requirements, which are detailed in contracts or equivalent agreements, are (1) the use of proven methods of analysis, (2) the use of specified materials for the calibration of analytical methods, (3) the successful analysis of test samples at stated levels of accuracy and precision, and (4) the use of a detailed (and documented) internal quality assurance program.

Approved methods of analysis are those published in an ERDA document. These methods, summarized in Table II, were proven adequate by the analysis of test samples among ERDA contractor and license facilities in two extensive round robin programs. Other methods of analysis may be approved by HEDL based on demonstrated capability equivalent to the approved methods.

The use of well-characterized calibration materials is essential to obtaining accurate chemical results. Further, the use of the same calibration materials by all participating laboratories reduces shipper-receiver differences. Standard Reference Materials of the National Bureau of Standards for uranium and plutonium, certified for assay and isotopic distribution values, are the only well-characterized reference materials available and are specified for this program. For metallic and nonmetallic impurities, LASL prepared powder blends in the three matrices of uranium-plutonium mixed oxide, plutonium oxide, and uranium oxide are used in the program. Calibration materials are not available for water content, gas content, and total volatiles, because materials with long-term stability are not easily obtainable. For these three determinations and for the O/M determinations, the analysis methods are specified in detail. Prior to using the methods for analysis of production materials, the laboratories calibrate with the specified materials, then reverify the calibration factors on a weekly basis. Control charts are maintained and a recalibration is done when an "out of control" situation exists. Whenever a method has not been in use for a 90-day period, a specified number of quality control samples must be successfully analyzed by the laboratories in order to requalify. The number of samples is usually about four, and the statistical tests consider both accuracy and precision.

Each participating laboratory must maintain its own internal quality assurance program designed to demonstrate clearly that methods are in control at all times. This internal

TABLE II. APPROVED METHODS OF ANALYSIS

<u>Specification Component</u>	<u>Chemical Method</u>
Plutonium Assay	Controlled Potential Coulometry
Uranium Assay	Controlled Potential Coulometry
Plutonium - Uranium Isotopic Composition	Thermal Ionization Mass Spectrometry following Ion Exchange Separation
Americium - 241	Gamma Counting in Well-Type NaI(Tl) Detector
O/M Ratio	Thermogravimetry
Chloride	Pyrohydrolysis - Coulometric Silver Titration
Fluoride	Pyrohydrolysis - Ion Selective Electrode
Carbon	Ignition to CO <sub>2</sub> - Gas Chromatography
Nitrogen	Steam Distillation as NH <sub>3</sub> - Colorimetry
Sulfur	Distillation as H <sub>2</sub> S - Colorimetry
Phosphorus	Solvent Extraction - Colorimetry
Metal Impurities	Emission Spectrography for all Except Tungsten by Colorimetry
Trace U in PuO <sub>2</sub>	Colorimetry following Ion Exchange Separation
Water	Volatilization - Electrolytic Cell
Gas Content	Induction Heating - Gas Volumetric Measurement
Total Volatiles	Weight Loss upon Heating

program must include a documentation system that provides for traceability of each reported result back to raw laboratory data from which the result was obtained. The system must provide for identification and control of each sample from the time it is received by the laboratory until all required analyses are completed. All data obtained from calibration and control standards must be recorded and be easily retrievable from the system. The internal program must include provisions for qualifying analysts. Criteria to establish qualification and a system for certifying and documenting qualification must be included. Provisions must be included in the program for calibrating and controlling all equipment that affects the quality of measurements. These provisions should include tolerance requirements for volumetric glassware and for weights used to calibrate balances. Requirements for the quality of reagents used, the labeling of standards and reagents, and their storage must be included.

Each laboratory must have written procedures for implementing the requirements of its internal quality assurance program. Included is the requirement that all analytical methods used to make analyses must be in written form. The format used for writing the methods must include, as a minimum, the following information: brief summary of the method; recommended sample size and range of the method; interferences; equipment, reagents, and standards required; calibration procedure; step-by-step procedure for the analysis including precautions; and a calculation procedure.

#### CALIBRATION AND QUALITY CONTROL MATERIALS

Prior to the start of this program, LASL presented a paper at the 1971 IAEA Symposium "Analytical Methods in the Nuclear Fuel Cycle", [1], in which the techniques used to prepare the calibration and quality control materials were described. We will briefly review these techniques and give a description of subsequent operations. These include the packaging of materials, the assignment of control limits to the quality control materials, and record-keeping practices.

The calibration and quality control materials used in this program are summarized in Table III. The blends of nonmetallic impurities and of metallic impurities are prepared in the three matrices of mixed oxide, uranium oxide, and plutonium oxide. This is necessary because the participating laboratories segregate their areas (and apparatus plus personnel) by material composition. The blending procedures are given in reference [1]. The mixed oxide and  $\text{UO}_2$  pellets used as quality control materials are discrete batches<sup>2</sup> for which random sampling and analyses have verified homogeneity.

TABLE III. CALIBRATION AND QUALITY CONTROL MATERIALS

<u>Measurement</u>	<u>Calibration Material</u>	<u>Quality Control Materials</u>
Plutonium Isotopic	NBS SRM 948	Mixed Oxide Pellets, and Pu Oxide
Uranium Isotopic	NBS SRM U-010	Mixed Oxide Pellets, and UO <sub>2</sub> Pellets
Plutonium Assay	NBS SRM 949	Mixed Oxide Pellets, and Pu Oxide
Uranium Assay	NBS SRM 950 or 960	Mixed Oxide Pellets, and UO <sub>2</sub> Pellets
Am-241	None	None <sup>(a)</sup>
O/N Ratio	None	Mixed Oxide Pellets, and UO <sub>2</sub> Pellets
Carbon, Chloride, Fluoride, Nitrogen, Sulfur, Phosphorus, Tungsten	Blends in Mixed Oxide, U Oxide, and Pu Oxide	Blends in Mixed Oxide, U Oxide, and Pu Oxide
Metal Impurities	Blends in Mixed Oxide, U Oxide, and Pu Oxide	Blends in Mixed Oxide, U Oxide, and Pu Oxide
Trace U in PuO <sub>2</sub>	Characterized Pu Oxide	Characterized Pu Oxide

(a) The Am-241 level of production material normally is computed based on the measured Pu-241 content and the age of the material since purification.



A calibration series of metallic or nonmetallic impurities consists of five blends in which the concentrations of the impurities range from one-tenth to twice the specification values. Generally, the concentration levels of the impurities in quality control samples range from one-half to slightly above the specification value because the decision to accept or reject manufactured material is most critical at this level. Six different quality control blends are concurrently in circulation, with the differences in the concentration levels of the measured components being so slight, that the larger random error of the analytical method discourages attempts to establish blend identity.

Blends are analyzed to verify that no errors, such as incorrect weighings, were made and that homogeneity was attained. At least four random samples of each blend are analyzed in duplicate.

Except for carbon-containing blends, the primary packaging container is polyethylene or polystyrene. Random samples of container batches are analyzed by neutron activation with emphasis placed on chlorine. Because the materials abrade plastic containers, those designated for carbon measurements are packaged in glass containers with screw-on plastic lids. A lead insert is placed in the lid to prevent material contacting the plastic. All materials containing plutonium have a second outer plastic container. The packaging is done in a manner which precludes surface contamination. The labels of all materials are placed on the inner container. Special packaging is required for mixed oxide pellets that serve as quality control material for the O/M measurements. From the time of their preparation, the pellets are maintained in an argon atmosphere to maintain their hypostoichiometric oxygen level. Individual pellets are packaged in glass ampoules in an argon-atmosphere glovebox. The ampoule is sealed by applying vacuum and heating in a chamber with the heat produced by a current flowing through a nichrome-wound element.

The assignment of control limits to the prepared quality control blends is somewhat subjective. Although the matrix materials of mixed oxide, plutonium oxide, and uranium oxide are selected, based on analyses, for low levels of the added impurities, the levels of certain impurities are significant relative to the added levels. Also, the uncertainty of the analyses is relatively large at low concentration levels, approaching the detection limit of the analytical method. The control limits assigned to the value of a component are approximately two standard deviations, including the analytical uncertainty, the propagated error of the blending preparation, and the uncertainty of the concentration of the components in the matrix material.

The general relationship is:

$$\text{Upper Control Limit} = \left(1 + \frac{2E_Q}{100}\right) \left(1 + \frac{E_B}{100}\right) (A+R+E_R)$$

$$\text{Lower Control Limit} = \left(1 - \frac{2E_Q}{100}\right) \left(1 - \frac{E_B}{100}\right) (A+R-E_R)$$

where

$E_Q$  = Relative standard deviation, in %, of the analytical method, computed from previous interlaboratory sample exchange programs.

$E_B$  = Propagated error of blending preparation, relative standard deviation, in %.

$A$  = Added level of component.

$R$  = Measured level of component in matrix material.

$E_R$  = Standard deviation associated with  $R$ .

For example, in a mixed oxide blend for nitrogen

$$E_Q = 30\%$$

$$E_B = 2\%$$

$$A = 80 \text{ } \mu\text{g/g}$$

$$R = 20 \text{ } \mu\text{g/g}$$

$$E_R = 10 \text{ } \mu\text{g/g}$$

$$\text{Upper Control Limit} = 180$$

$$\text{Lower Control Limit} = 35.$$

The quantity of record keeping associated with the calibration and quality control materials is extensive. All blend preparation data are recorded in notebooks which are signed by two chemists. The one preparing the blends and a supervisor or co-worker must sign for every recorded weighing measurement or other critical operation. The computation of blend values and the overcheck analytical results are also recorded. Every shipment of material to a participating laboratory is accompanied by a detailed listing of the individual vials of materials, including the plutonium accountability value. The values of the calibration materials are also provided. Finally a detailed list of the code information for the quality control samples (including the unique number of each vial), the container blend designation, and the control limits is provided solely to the administrator of the quality assurance program at HEDL.

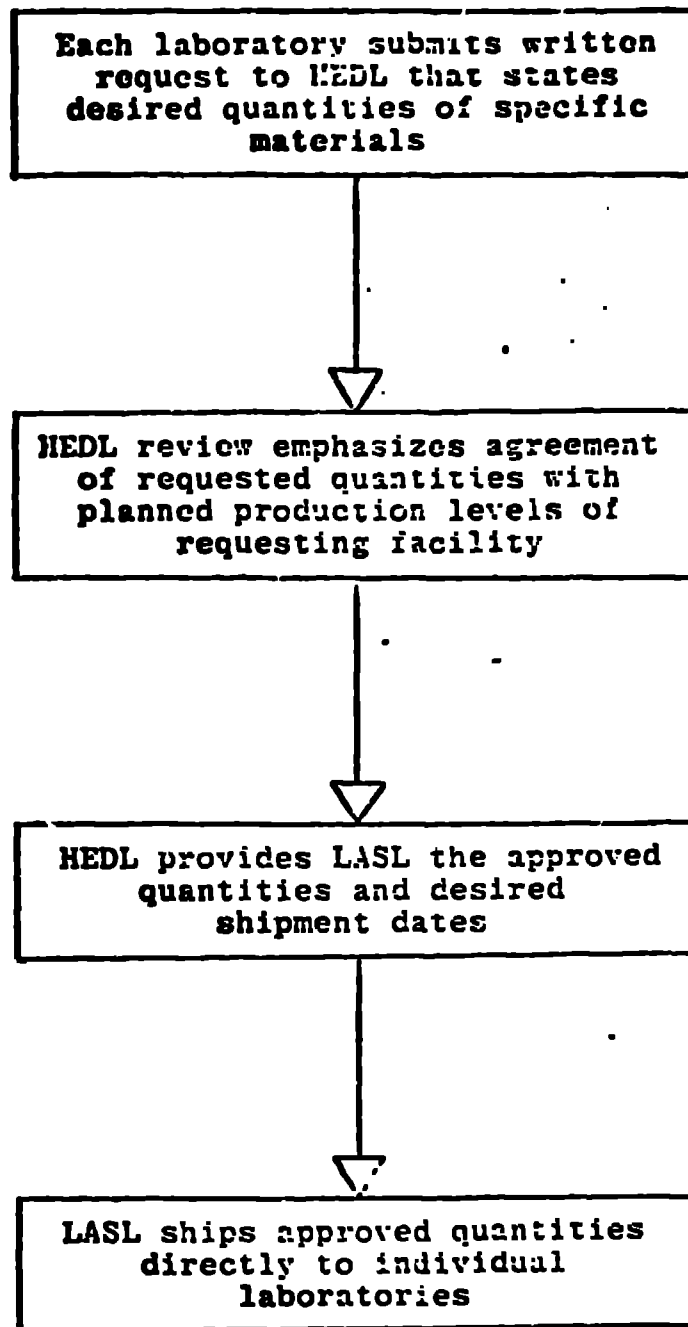
## ADMINISTRATION OF THE PROGRAM

The overall administration of the program is assigned to one person in the HEDL Quality Assurance Department. This centralized responsibility has provided ready communications among the participating laboratories, producing coordinated efforts and resolutions of problems. The administrative functions include (1) the qualification of laboratories as discussed previously, (2) the approval of calibration and quality control material shipments from LASL to the participating laboratories, (3) the continuous surveillance of laboratory operations, including a major task of recording all results obtained on quality control samples, and (4) continuous review, using charts and statistical tests, of the recorded quality control data.

The operations associated with the calibration and quality control material shipments are presented in Fig. 1. Normally, shipments are made at three month intervals. To provide LASL with guidance and lead time, necessary to the effective planning of material preparation and packaging, each laboratory submits a written request to HEDL stating the types and quantities of calibration and quality control materials desired for a year of operation. The preparation of these materials, described earlier, requires considerable time and effort and is costly. The HEDL review, therefore, emphasizes that the requested quantities agree with the planned production levels of the requesting facility. HEDL then informs LASL of the approved quantities and desired shipment dates. The shipments are made from LASL directly to the individual laboratories.

The best assessment of a laboratory's performance is attained by the analysis of quality control samples that are supplied by, and statistically evaluated by, an organization independent of the laboratory. As outlined in Fig. 2, three independent organizations are involved: LASL as the supplier of the materials, the Quality Assurance Department of HEDL, and the Quality Assurance Department of each facility. Also, a Site Representative from HEDL is assigned to each facility. As stated previously, the code information and control limits for quality control materials are provided by LASL solely to the HEDL Quality Assurance Administrator. He provides his Site Representative with information appropriate to the specific facility. The Site Representative, in turn, provides the facility's Quality Assurance Department with a partial listing of the information. This latter organization submits most of the quality control samples and maintains the surveillance.

The rate of analyzing quality control samples varies, based on past operating capabilities, but can be as much as one sample per day per operating apparatus and/or analyst. Should a result fall outside the control limits, the analysis of production samples is stopped, and the cause is evaluated. A second quality control sample is then analyzed. If the second result



**Fig.1. Operations Associated with the Shipment of Calibration and Quality Control Materials.**

falls within the control limits, analysis of production samples can be resumed. If, however, the result is again outside the control limits, the laboratory must requalify. Approval to resume operation is granted only by the facility's Quality Assurance Department based on the successful analysis of quality control samples.

By withholding a portion of the quality control sample code information, the Site Representative is provided the means to obtain an independent evaluation of a laboratory's performance. As shown in Fig. 2, the results obtained on quality control samples submitted by the facility's Quality Assurance Department are sent to the Department, as well as to the HEDL Site Representative and to the HEDL Quality Assurance Administrator. All quality control results go to the HEDL Quality Assurance Administrator, who overviews the operations as they occur in all laboratories. Statistical tests are used to assess problem areas unique to one laboratory or common to all laboratories.

Histograms provide among-laboratory comparisons and indicate whether the distributions of quality control sample results are normal, skewed, multimodal, or other. The histograms of quality control sample results, Fig. 3, for the O/M measurement of mixed oxide by three laboratories show a slightly skewed distribution for laboratories B and C, with laboratory A having a smaller range than the other two laboratories.

Conventional quality control charts, in which results for quality control samples are plotted by production lot, may show bias trends. Especially useful, as shown in Fig. 4, are plots of moving averages. This example, for the measurement of the plutonium content of mixed oxide, shows a trend to lower values for one quality control material by two laboratories.

Examples of a third type of chart are presented in Figures 5 through 7. These bar charts plot the results of quality control samples for all laboratories and are designed to differentiate unique laboratory difficulties, or problems common to two or more laboratories. The results are plotted on a percentage scale, in which the range of 100% between the upper and lower limits represents four standard deviations (  $\pm 2$  standard deviations from the stated value) and the stated value of the quality control material is set at 50%. Fig. 5 presents results for the plutonium content of a mixed oxide quality control material. All laboratories are in control for this material. Fig. 6 illustrates a case where the average result obtained by each of the four laboratories for the carbon content is higher than the stated value. Laboratories A and B have precision difficulties. In the last example, Fig. 7, a rather complex situation exists. All laboratories tend to have biased results, high for laboratory A, and low for the other three laboratories. The precisions of all four laboratories are comparable.

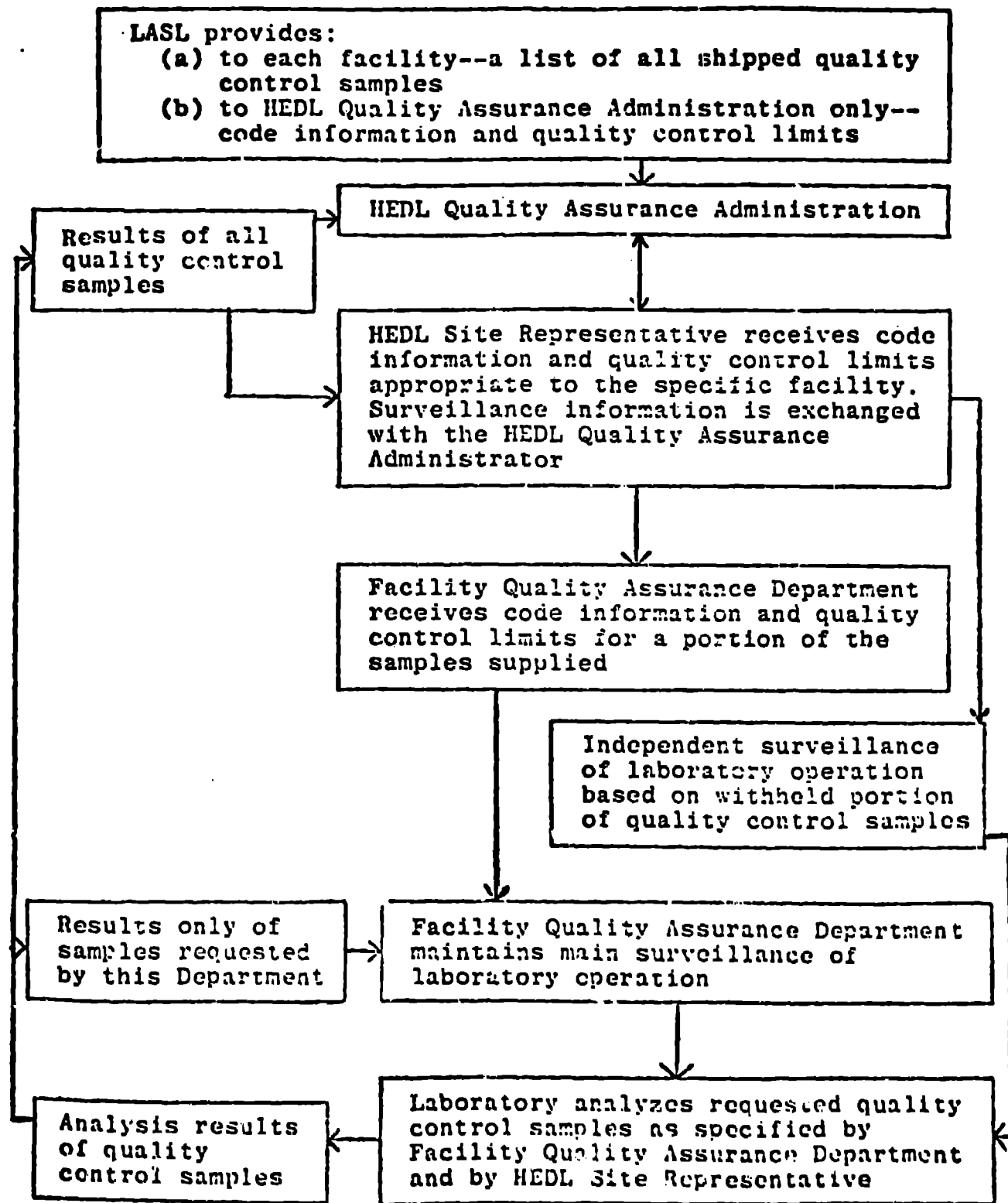


Fig.2. Quality Control Sample Distribution and Flow of Data Results.

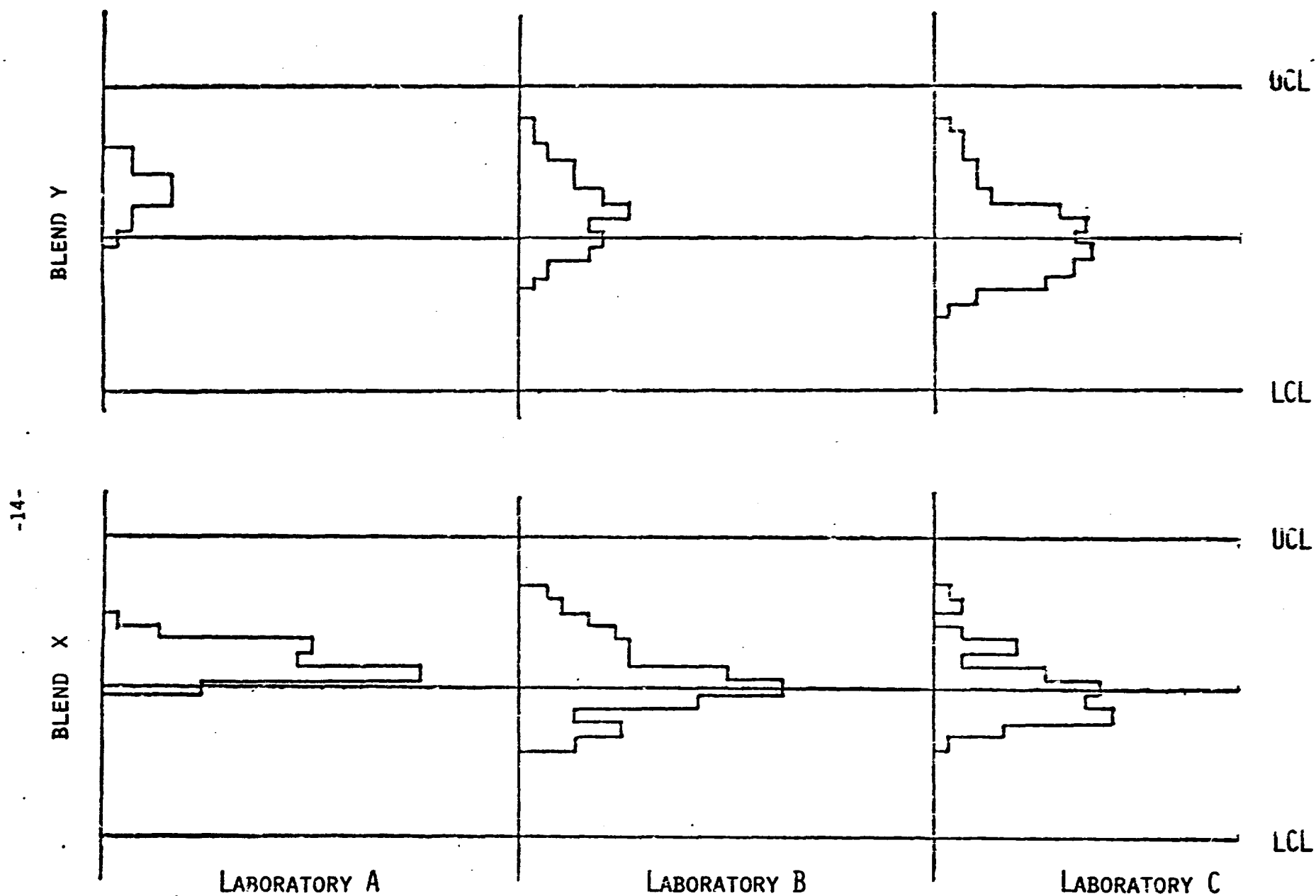


FIG.3. HISTOGRAMS OF THE RESULTS OBTAINED FOR THE O/M RATIO OF TWO QUALITY CONTROL MIXED OXIDE MATERIALS BY THREE LABORATORIES.

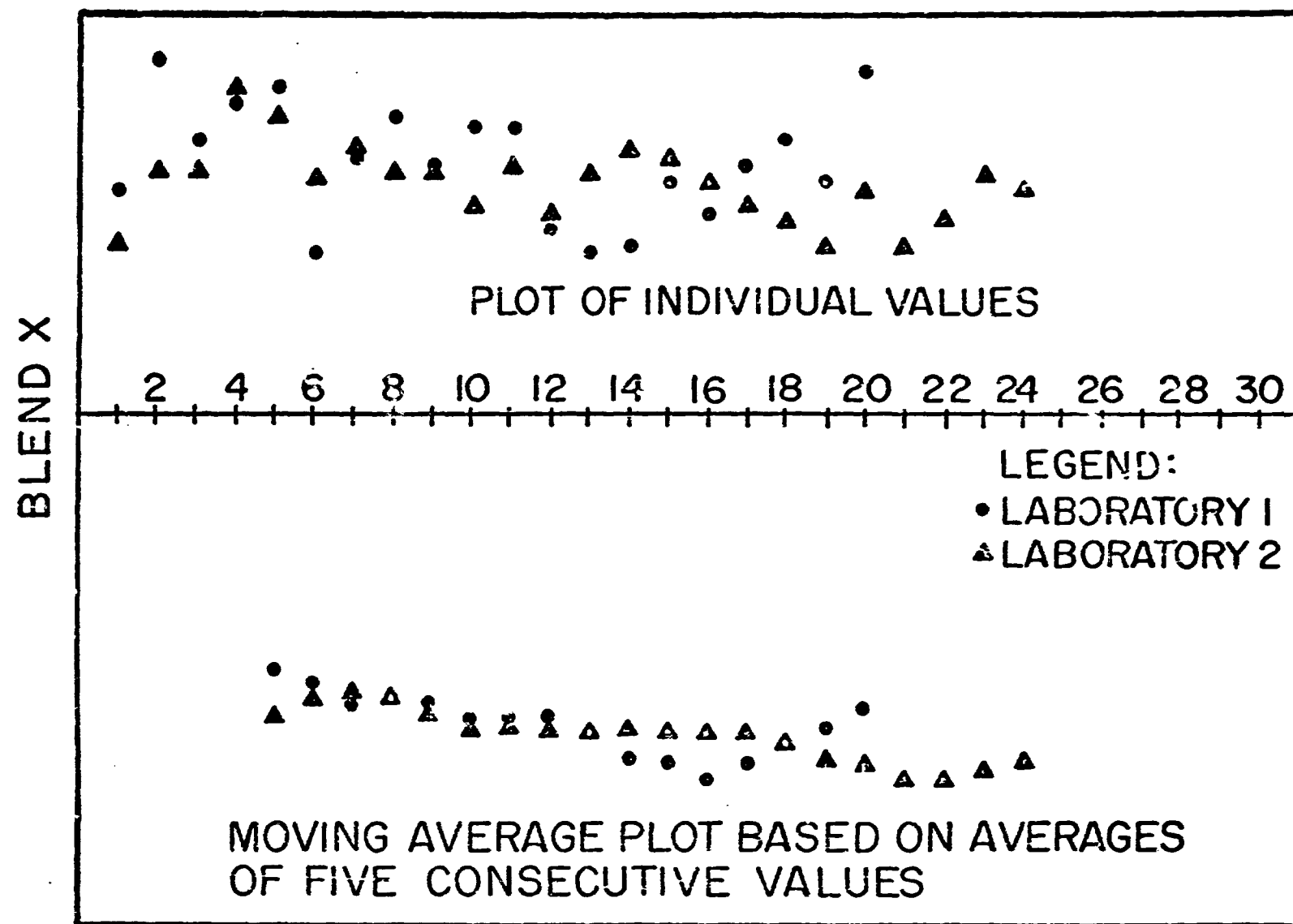


FIG.4. PU WT% IN MIXED OXIDE.



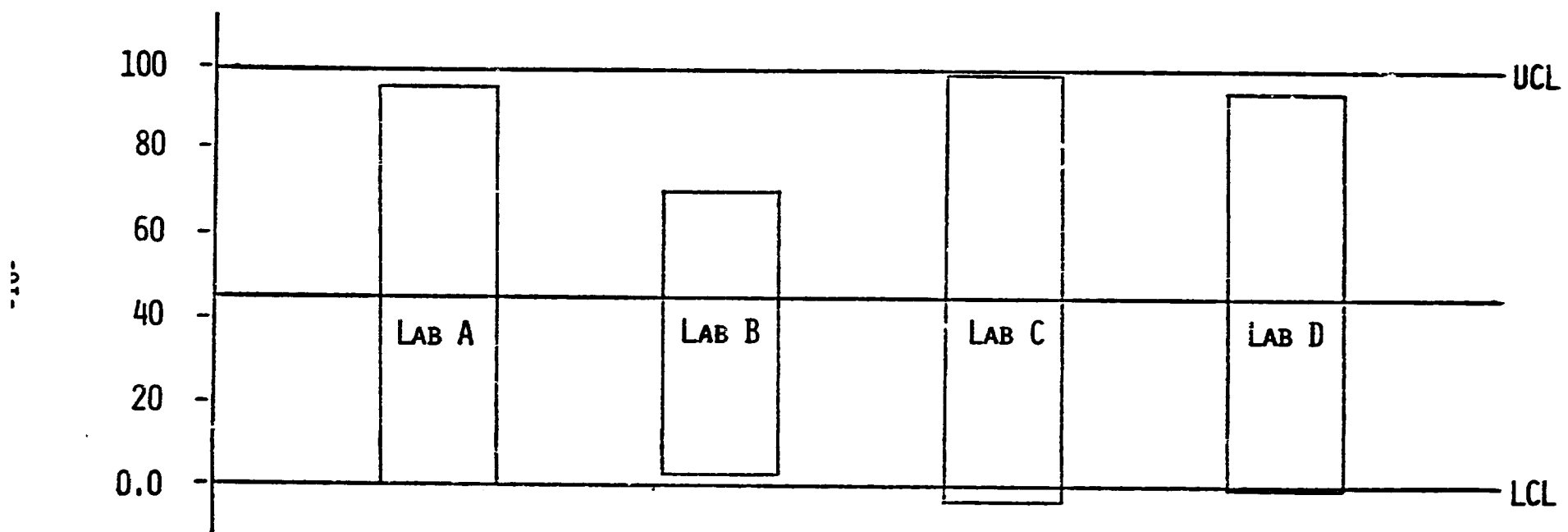


FIG.5. BAR CHART FOR THE RESULTS OBTAINED FOR THE PLUTONIUM CONTENT.

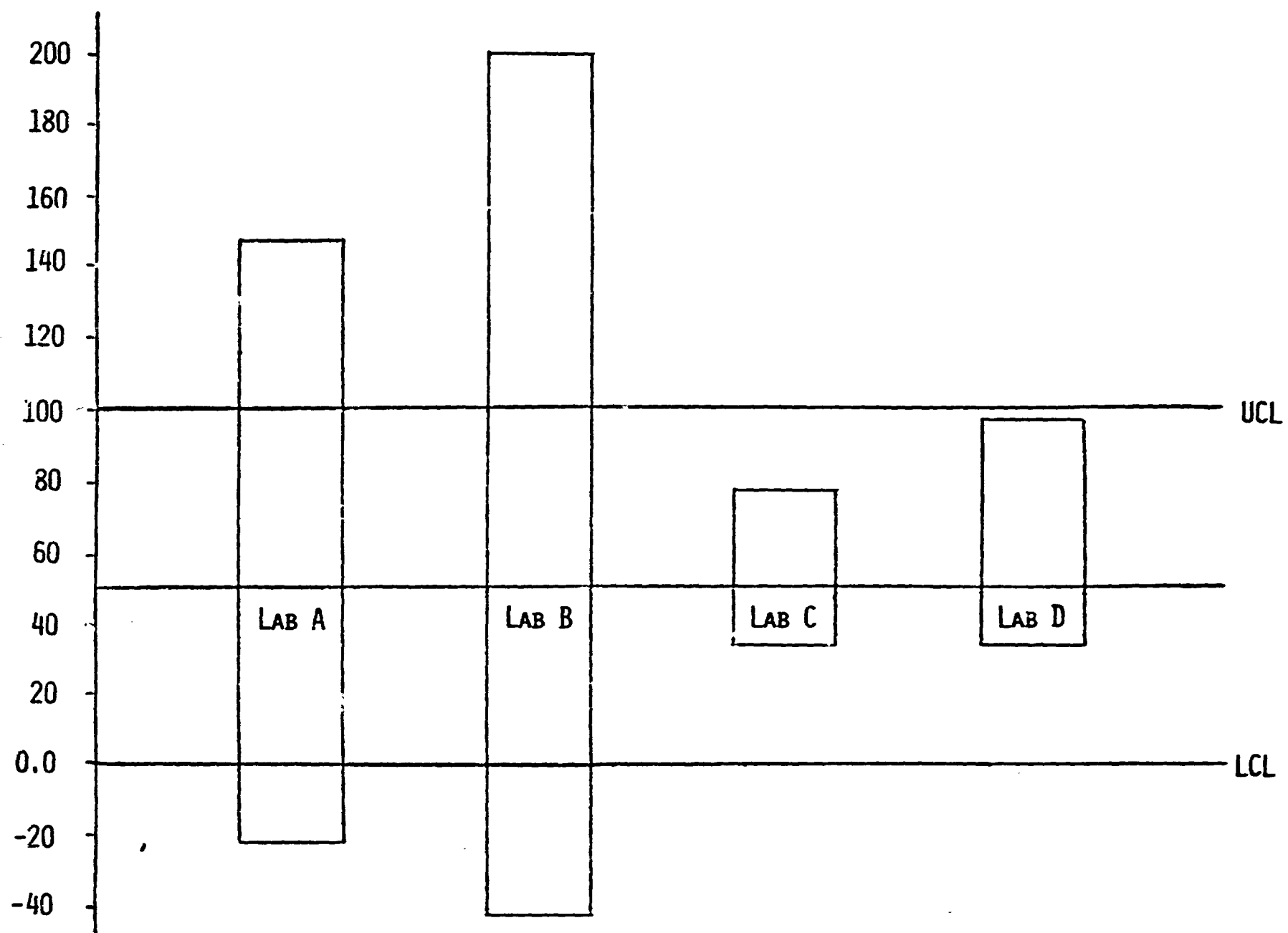


FIG.6. BAR CHART FOR THE RESULTS OBTAINED FOR THE CARBON CONTENT.

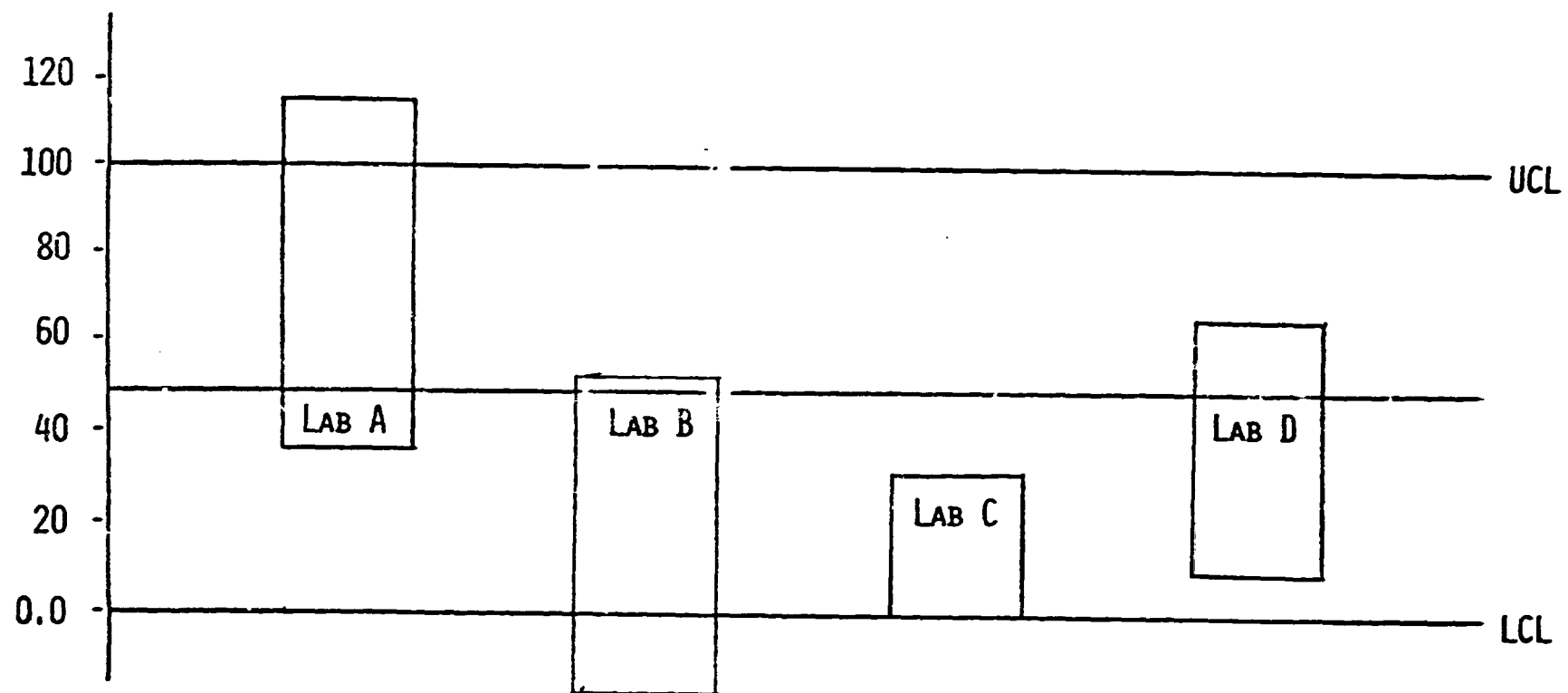


FIG.7. BAR CHART FOR THE RESULTS OBTAINED FOR THE CHLORIDE CONTENT.

### OPERATIONAL EXPERIENCES

As expected, difficulties were more noticeable at the beginning of the program. Difficulties occurring in individual laboratories were traced to inadequate training of personnel, defective equipment, and reagent or atmospheric contamination. Initially, most laboratories experienced qualification difficulties for one or several methods and required some time to attain complete qualification.

From time to time, the data charting indicated a faulty quality control material. In one case, high bias chloride results were traced to the use of new containers for the packaged material in which the plastic cap liners were found to be vinyl chloride. In another case, high carbon results for one quality control material were found to have been caused by the use of a low value for the level of carbon in the matrix material used in the blend preparation.

An example of atmospheric contamination was high results for fluoride caused by concurrent use of a glovebox complex for fluoride and nitrogen determinations. The dissolution reagent for the nitrogen determination contained hydrofluoric acid. In another example, high results for silver were traced to the use of the same facility for another spectrographic method in which silver chloride carrier was used.

In one laboratory, a spectrographic method in use for the determination of rare earths went out of control. A combination of new personnel and the inadequacy of a separation procedure were determined to be the cause of loss of control. Retraining of personnel with emphasis on extraction techniques corrected the problem and the laboratory was requalified.

### CONCLUSIONS

This extensive quality assurance program, concerned with analytical laboratory performance for the FFTF fuel production, has provided the high quality fuel for which it was designed. Initially, the involved facilities were averse to the program, since it required about 10% more effort relative to the production material analyses. However, it soon became apparent this cost was more than offset by the confidence one had in the analytical results. This was due primarily to the use of common calibration materials and the surveillance by a quality assurance organization independent of the analytical laboratories. As personnel demonstrated a competence in analyzing quality control samples, a strong sense of work interest and pride developed. Most importantly the three years of operating history has demonstrated a low rate of between-laboratory differences which often require long and costly investigations.

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